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Dispersive Liquid–liquid Microextraction Combined with Laser-Induced Breakdown Spectrometry and Inductively Coupled Plasma Optical Emission Spectrometry to Elemental Analysis

I. Gaubeur[a*], M.A. Aguirre[b], N. Kovachev[b], M. Hidalgo[b], A. Canals[b]

[a]*Human and Natural Sciences Center – Federal University of ABC, Av. dos Estados, 5001, 09210-971, Santo André, São Paulo, Brazil*

[b]*Department of Analytical Chemistry and Food Science and University Materials Institute – University of Alicante, Apdo. 99, Alicante E-03080, Spain*

Abstract

In this paper, two analytical methodologies based on the combination of dispersive liquid-liquid microextraction with inductively coupled plasma optical emission spectrometry and laser-induced breakdown spectrometry, respectively, were evaluated for simultaneous preconcentration and detection of Cd, Co, Ni, Pb and Zn. The microextraction procedure was based on the injection of appropriate quantities of 1-undecanol and methanol into the sample solution containing the complexes formed between metal ions and 1-(2-pyridylazo) 2-naphtol (PAN). The main experimental factors affecting the complexation and the extraction of metals (pH, PAN concentration, salt addition and extractant solvent and disperser solvent volume) were optimized using a multivariate analysis consisting of two steps: a Plackett-Burman design followed by a Circumscribed Central Composite Design (CCCD). Under optimum microextraction conditions, the analytical features of the proposed methodologies were assessed. Accuracy was evaluated by analyzing two certified reference materials, yielding results in agreement with the certified values. Both methodologies were applied to the analysis of a number of beverage samples.

Keywords: Laser-Induced Breakdown Spectrometry; Inductively Coupled Plasma Optical Emission Spectrometry; Dispersive liquid-liquid microextraction; Trace elemental analysis.

[*] Corresponding authors.Tel.: +55 11 4996 0187
E-mail addresses: ivanise.gaubeur@ufabc.edu.br (I. Gaubeur); montserrat.hidalgo@ua.es (M. Hidalgo).

1. Introduction

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), Flame Atomic Absorption (FAAS), Electrothermal Atomic Absorption Spectrometry (ETAAS), molecular spectrophotometry and other atomic and molecular conventional instrumental techniques have all been extensively used to quantify metals in many samples. Laser Induced Breakdown Spectroscopy (LIBS), even if not yet considered a conventional instrumental technique, has also been used for elemental analysis since its introduction, providing a significant number of applications [1-4].

Irrespective of the recent advancements in analytical instrumentation, extraction and preconcentration procedures prior to the detection step are still necessary, either for decreasing detection limits or for eliminating matrix effects [5-13].

The use of procedures resulting in low consumption of reagents and, consequently, in drastically reducing residue discharge, has been an attractive field of research for the development of analytical methods tied to environmental-friendly analytical chemistry [14-16]. As a consequence, traditional extraction procedures are being increasingly replaced by microextraction methodologies, which are nowadays widely used for analyte separation and enrichment. Among others, dispersive liquid-liquid microextraction (DLLME) is a liquid-liquid extraction procedure that allows for a low consumption and discharge of chemical reagents. It is based on the mixing of an extractant solvent and a disperser solvent (with high miscibility in both aqueous and organic media). The quick addition of an appropriate mixture of these two solvents into the sample leads to the formation of a great number of small droplets of extractant solvent, which remain dispersed in the aqueous solution. As a result, analyte is extracted to the extractant solvent droplets (generally hydrophobic organic compounds), which is then separated from the aqueous phase by centrifugation. Some advantages of DLLME are operation easiness, quickness, low cost and high recovery factors and preconcentration [17-20].

Different conventional atomic spectrometric techniques have been already combined with DLLME for trace-metals analysis. Among them, ETAAS has been, by far, the most widely used due to its requirement of microamounts of sample for analysis [12]. In contrast, few papers propose the combination of this microextraction technique with ICP-OES, probably due to the intrinsic difficulties of this analysis method of organic matrices [21-25].

LIBS, as ETAAS, only needs a very low quantity of sample for analysis. Moreover, this technique presents some other added advantages, such as quick multi-elemental determination and possibility for *in situ* analysis. This technique can be used for direct analysis of gases, liquids and solids. However, its low sensitivity when compared to other atomic spectrometry techniques constitutes the most important limitation for (ultra) trace elemental analysis, especially for liquid samples [1,26,27]. Aguirre et al. [26] proposed the combination of LIBS with microextraction techniques as a method to extend the applicability of LIBS to trace elemental analysis in liquid samples. The capability of the technique to analyze microvolumes of sample was tested by evaluating two different experimental strategies for LIBS analysis: (i) direct laser irradiation of microdroplets suspended from the tip of a microsyringe and (ii) analysis by laser irradiation of microdroplets dried on metallic substrates (surface-enhanced LIBS - SENLIBS). Jesus et al. [28], using the combination of DLLME and LIBS, developed a method for the determination of V and Mo. The proposed method was applied to the analysis of different real samples (*i.e.*, pharmaceutical, multimineral formulation, soil and mineral water) and a beef liver reference material.

In this context, the aim of this work was, on the one hand, to propose a DLLME method based on the use of 1-undecanol (extractant solvent) and methanol (disperser solvent) for extraction of metal ions as 1-(2-pyridylazo) 2-naphtol (PAN) complexes and, on the other hand, to evaluate the combination of the proposed DLLME procedure with ICP-OES and LIBS techniques (*i.e.,* DLLME-ICP OES and DLLME-LIBS) for trace elemental analysis of liquids samples. To this end, the main experimental factors affecting the DLLME of several metals (Cd, Co, Ni, Pb and Zn) were optimized using a multivariate analysis. Under optimum DLLME conditions, analytical figures of merit of the DLLME-ICP-OES and DLLME-LIBS combinations were estimated. Accuracy of the proposed methods was evaluated from the analysis of two Certified Reference Materials (estuarine water and hard drinking water). Finally, several beverage samples (drinking water, alcoholic beverages and soft drink) were analyzed in order to assess the applicability of the methods to real samples analysis.

2. Material and Methods

2.1 Instrumentation

A pH meter (model Basic 20+, Crison Instrument, Barcelona, Spain) with a combined glass electrode was used for pH measurements. A centrifuge (model 2690/5, Nahita Centrifuges, Beriain, Spain) was used to accelerate the phase separation. The disperser and extractant solvent mixture was added to the sample using a 1000 µL syringe (Gastight®, Hamilton Co, Reno, Nevada, USA).

An inductively coupled plasma-optical emission spectrometer (model 720-ES, Agilent Technologies, Melbourne, Victoria, Australia) was used for ICP-OES measurements. Table 1 shows the instrumental parameters used and the emission lines evaluated with this system.

For LIBS analysis, the laser-induced plasmas were generated in air at atmospheric pressure by focusing a 10 Hz pulsed Nd-YAG laser (model HYL Handy-YAG, Q-switched, Quanta System S.P.A., Varese, Italy), emitting a pulse of energy 180 mJ (pulse width 10 ns FWHM) at 1064 nm, on the sample to analyze. The laser beam was focused on the micro samples by a biconvex lens with a 100 mm focal length. Plasma emission was collected and sent, through a five-furcated optical fiber (5x400 µm fiber optic cable, model FC5-UV400-2, Avantes, Eerbeek, Netherlands), to the entrance slit of a five-channel spectrometer (model AvaSpec-2048-SPU, Avantes, Eerbeek, Netherlands) where plasma's light was spectrally resolved and detected. A delay system consisting of two pulse generators (digital delay/pulse generator, model DG 535, Stanford Research Systems, Inc. and 1 MHz–50 MHz pulse/function generator, model 8116A, Hewlett Packard/Agilent Technologies, Santa Clara, USA) was used for synchronization of laser firing and data acquisition. Spectra were collected 1.3 µs after the plasma generation, with 1 ms acquisition time. Cd I (214.44 nm), Ni I (352.54 nm) and Zn I (202.55 nm) were the emission lines evaluated with this system. LIBS spectra were processed using the spectroscopic software LIBS++®, v. 3.12.4.1., IPCF-CNR (Pisa, Italy).

2.2 Reagents and solutions

All solutions were prepared with analytical grade chemicals and deionized water obtained from Milli-Q system (Millipore, Bedford, USA). A 2.3 x 10^{-3} mol L^{-1} PAN

stock solution was prepared by dissolving appropriate amounts of reagent (Sigma Aldrich, St. Louis, USA) in absolute ethanol (Sharlau, Sentmenat, Spain). Buffer solutions were prepared from acetic acid (Merck, Darmstadt, Germany) and sodium hydroxide (Merck, Darmstadt, Germany) at pH 3.5, 4.5 and 5.0, ammonium acetate (Merck, Darmstadt, Germany) at pH 7.0, ammonia solution 32% (Sharlau, Sentmenat, Spain) and ammonium chloride (Panreac Químicas S.A., Castellar del Vallès, Spain) at pH 9.5 and 10.5. Ethanol, methanol, acetone and acetonitrile (Sigma Aldrich, St. Louis, USA) were used as disperser solvent and 1-undecanol (Acros Organics, Geel, Belgium) as extractant solvent. Cadmium, cobalt, nickel, lead and zinc standard solutions were prepared by appropriate dilutions of 1,000 mg L^{-1} monoelemental aqueous stock solutions (High-Purity mono-element standard solutions, Charleston, UK).

2.3 Samples

Two certified reference materials (CRM) from European Reference Material (ERM): Estuarine water (LGC6016) and Hard drinking water (ERM® CA011a), both furnished by the Laboratory of the Government Chemist (LGC, Teddington, Middlesex, UK), were analyzed to assess methods accuracy.

Several beverages purchased from a local market: Drinking water, two alcoholic beverages (obtained by distillation of fermented fruit and brand whisky - both containing 40-60% alcohol) and a soft drink, were also analyzed to evaluate the applicability of the methods to real samples.

2.4 DLLME procedure

For extraction of the analytes by DLLME, different amounts of sample or standard solutions were transferred to 10-mL glass tubes. An excess of chelating agent PAN was added to the solution, ethanol absolute and buffer solution (NH_4OH/NH_4Cl pH 9.0) were added - maintaining final ethanol percentage at 28%. After a complexation time of around 15 min [13], the mixture was filled with deionized water up to 9 mL. A mixture of 70 µL of extractant solvent (1-undecanol) and 150 µL of disperser solvent (methanol) was added using a glass syringe. Phase separation was then achieved by centrifugation at 3,000 rpm for 3 min. The organic phase was retrieved with a micropipette for ICP-OES and with a microsyringe for LIBS analysis.

For ICP-OES detection, around 40 µL of the analyte-enriched solvent was diluted to 100µL with 1-propanol in order to reduce viscosity and increase the

nebulization efficiency [25]. The diluted solution was then analyzed by the ICP-OES spectrometer using the experimental conditions shown in Table 1.

LIBS analysis was carried out using the surface-enhanced LIBS methodology (SENLIBS) already described elsewhere [26]. To this end, 10 µL of the solution was transferred on an aluminum substrate, heated to dryness and analyzed by the LIBS experimental system described above (Section 2.1).

3. Results and discussion

3.1 Optimization of DLLME procedure

The main experimental factors affecting metals extraction using DLLME (pH, PAN concentration, salt addition ($NaNO_3$), extractant solvent volume and disperser solvent volume) were optimized using a multivariate analysis consisting in two steps: (i) a Plackett-Burman design (screening) followed by (ii) a Circumscribed Central Composite Design (CCCD) (optimization) using the NemrodW statistical software (NemrodW® v.2007/2010, LPRAI, Marseille, France). This study was carried out using ICP-OES as detection technique and a model sample containing 50 µg L^{-1} in the different analytes.

In the screening study, the maximum (+) and minimum (-) values selected for the different factors were: pH (+) 9.0 and (-) 5.0, PAN concentration (+) 130 µmol and (-) 50 µmol, $NaNO_3$ concentration (+) 4.0% and (-) 0.0%, extractant solvent (1-undecanol) volume (+) 100 µL and (-) 50 µL and disperser solvent (ethanol) volume (+) 250 µL and (-) 150 µL. The Plackett-Burman experimental matrix generated 12 experiments, which resulted in the Pareto charts shown in Fig. 1 (a-e). In these figures, white bars indicate variables presenting a significant effect on DLLME procedure, while non significant variables are indicated by black bars. On the other hand, bars to the right indicates favorable DLLME conditions at higher values of that variable (*i.e.*, positive effect), while the opposite (*i.e.*, favorable conditions at lower values of the variables, negative effects) are indicated by bars to the left. The Pareto charts also include two vertical reference lines corresponding to the 95% confidence level.

It can be noticed from Fig. 1 (a-e) that, in general, DLLME was favored at low values of extractant solvent volume and high pH values. Salt ($NaNO_3$) addition, PAN concentration and disperser solvent volume proved to be no significant in the DLLME procedure. The evaluation of pH value is critical in metal extraction procedures, mainly

due to its influence on the complexation step. In the particular case of PAN, which has been previously used as chelating agent in microextraction procedures [30-33], pH values below 3.35 favors the protonated form of PAN ((pKa LH_2^+ = 3.35 at 25 ^oC) [34]), therefore limiting chelate formation. Moreover, high pH values could also have a negative effect on extraction, since hydrolysis of metals of interest may take place. The volume of extractant solvent has also a direct influence on microextraction. An increase in the extractant solvent volume leads to an increase in the final volume of organic phase in which analytes are extracted. Therefore, an excessive extractant solvent volume could lead to a dilution effect, thus decreasing the preconcentration factor [12,35].

Since extractant solvent volume and pH were found the only significant factors from the Plackett-Burman design, the optimization of these two variables was carried out using response surface methodology (RSM) through application of a CCCD. Therefore, disperser solvent (ethanol) volume and $NaNO_3$ concentration were fixed at their lower level, 150 µL and 0.0%, respectively. To guarantee an excess of complexing agent, PAN concentration was fixed at 260 µmol. The different level values chosen in CCCD were pH – 3.5; 4.5; 7.0; 9.5 and 10.5 - and extractant solvent volume – 50; 57; 75; 93 and 100 µL - which resulted in a matrix with 12 experiments. Response surfaces obtained for the different metals are shown in *Fig. S1* (Supplementary Material). Optimum pH and extractant solvent volume conditions for extraction of the different metals were: 9.3 and 74 µL for Cd; 8.4 and 74 µL for Co; 9.2 and 75 µL for Ni; 8.3 and 54 µL for Pb and 8.1 and 54 µL for Zn. On that basis, pH 9.0 and extractant solvent volume 70 µL were selected as the most favorable conditions for simultaneous DLLME of all five metals.

In summary, the DLLME experimental conditions selected were: PAN concentration 260 µmol, 70 µL of extractant solvent, 150 µL of disperser solvent and pH 9.0 (NH_4OH/NH_4Cl).

3.2 Selection of the disperser solvent type

In the previous optimization study, ethanol was selected as the disperser solvent; however, some other solvents such as acetone, acetonitrile (ACN) or methanol could be also used to this end. In this work, the use of 1-undecanol as extractant solvent in combination with these other possible disperser solvents was studied and compared with the use of ethanol. Figure 2 shows the signal improvement obtained for each metal

using different disperser solvents. Here, signal improvement was calculated as the ratio of the signal obtained in the ICP-OES analysis of the samples without and with the DLLME procedure (see Section 2.4). According to the results, the use of methanol as disperser solvent resulted in the highest signal improvement for the majority of the metals, followed by ACN, ethanol and acetone, which showed similar behavior. In view of these results, methanol was finally selected as the disperser solvent used for further studies.

3.3 Analytical features – ICP OES and LIBS detection

Analytical calibration curves were obtained with both ICP-OES and LIBS instrumental techniques. In both cases, standard solutions were analyzed in two different ways: without the DLLME procedure (*i.e.,* ICP-OES or LIBS analysis of the standard solutions), and with the DLLME procedure (*i.e.,* DLLME-ICP-OES or DLLME-LIBS analysis). All analytical curves were obtained from triplicate analysis of the standards. In DLLME-ICP-OES methodology, all analytes extracted (*i.e.,* Cd, Co, Ni, Pb and Zn) were investigated. However, DLLME-LIBS methodology was found to be unpractical for Co and Pd detection at concentration levels below 1 mg L^{-1}, being out of the scope of the present work (*i.e.,* trace metals analysis). Therefore, only Cd, Ni and Zn were investigated with this methodology.

Table 2 and Table 3 summarize the analytical characteristics of the tested DLLME-ICP-OES and DLLME-LIBS methodologies. Detection and quantification limits (LOD and LOQ) were estimated according to IUPAC recommendations at 99% confidence level [36]. Repeatability (RSD, relative standard deviations) was estimated from 10 independent measurements.

Regarding DLLME-ICP-OES methodology (Table 2), it was observed from comparison of the sensitivity values obtained from the analytical curves corresponding to the ICP-OES and DLLME-ICP-OES analysis of the standards, that the use of the proposed microextraction procedure leads to an increase in sensitivity for all metals tested (i.e., 56-times higher for Cd, 9.5-times higher for Co, 51-times higher for Ni and Zn and 14-times higher for Pb), allowing the quantification of most of these metals in samples such as drinking water, at the concentration levels established by WHO (World Health Organization) - 3 µg L^{-1} (Cd), 70 µg L^{-1} (Ni) and 3 mg L^{-1} (Zn) [37-39], by the Environmental Protection Agency (EPA) - 5 µg L^{-1} (Cd), 15 µg L^{-1} (Pb) and 5 mg L^{-1} (Zn) [40] or by the European Drinking Water Directive of The European Union Council

(EUC) - 5 μg L^{-1} (Cd) [41]. At present, concentration limit for Co in drinking water is neither regulated nor recommended by these regulatory agencies.

Table 3 shows the analytical characteristics achieved when LIBS is used as detection technique. The analytical features of both DLLME-LIBS and LIBS analysis are presented for comparative purposes. As expected, the analytical characteristics of DLLME-LIBS are worse than those obtained with DLLME-ICP-OES methodology (Table 2), due to the already well known lower sensitivity and reproducibility of LIBS compared to ICP-OES. However, as can be observed from Table 3 by comparing LIBS and DLLME-LIBS methodologies, the use of a DLLME procedure prior to LIBS detection leads to an increase in sensitivity of 9.6-times for Cd, 6.7-times for Ni and 6.5-times for Zn, which results in detection and quantification capability improvements. For instance, LOQ for Ni decreases from 170 μg L^{-1} (LIBS) to 78 μg L^{-1} (DLLME-LIBS), being this value quite close to the 70 μg L^{-1} maximum limit recommended by WHO [38]. Regarding Cd, a significant element from an environmental and toxicological perspective due to both genotoxic and carcinogenic damages at any exposure level, LOQ values decrease from 183 μg L^{-1} (LIBS) to 18 μg L^{-1} (DLLME-LIBS). This 10.2 fold LOQ improvement, even still insufficient to reach WHO (3 μg L^{-1}), EPA (5 μg L^{-1}) or EUC (5 μg L^{-1}) regulations, demonstrates the combination of LIBS with microextraction procedures as being the key for future studies aimed to extend the capability of LIBS technique to the quantification of analytes of interest at trace levels in liquid samples.

3.4 Accuracy evaluation and applicability of the methods to real samples analysis

It is important to outline that the optimization study was performed on a model sample prepared in deionized water. Possible matrix effects influencing DLLME procedure due, for instance, to competitive chelate formation with concomitant metals, or to preferential diffusion of such concomitant metals chelates into the organic phase, were not considered. In order to evaluate possible matrix effects, two water certified reference material containing Ca, Mg, K and Na, among others, as majority elements - estuarine water CRM (LGC6016) and hard drinking water CRM (ERM® CAO11a) [42,43] - were successfully analyzed by using the proposed DLLME procedure. Results of this evaluation are shown in Table 4. As can be seen, recovery values ranging from 88% to 104% and from 102% to 109% were obtained for DLLME-ICP-OES and DLLME-LIBS, respectively. According to a statistical *t*-test performed at a 95%

confidence level, no significant differences were found between determined and certified values, with both detection techniques in both certified reference materials.

Different beverage samples were also analyzed by DLLME-ICP-OES and DLLME-LIBS in order to evaluate the applicability of the methods to real samples. Firstly, accuracy of the DLLME-ICP-OES method for Cd, Co, Ni, Pb and Zn determination was assessed by recovery assays. To this end, the samples were analyzed before and after being spiked with 25.0 μg L^{-1} and 50.0 μg L^{-1} of the different analytes. As observed from Table 5, recoveries ranging between 91 to 111% for almost all analytes and samples were obtained, with the exception of Pb in alcoholic beverage (brand whisky) and soft drink. In these two samples, probably due to some matrix interference affecting the extraction of the analyte, recoveries were below 52%. Afterward, determination of Cd, Ni and Zn in the same beverage samples was performed by DLLME-LIBS (Table 6). Recovery values shown in this Table were calculated by comparing the DLLME-LIBS results with those obtained by DLLME-ICP-OES, taking this latter as reference values. As can be seen, the results obtained for Ni and Zn by both methods were in good agreement, with percent recoveries ranging from 87 to 113%. Although the concentration of Ni contained in the samples of drinking water, alcoholic beverage (brand whisky) and soft drink is within detection and quantification limits, a very good recuperation (99-102%) allows the acceptance of found concentration.

Determination of the same analytes in water samples by ICP-OES combined with microextraction procedures has also been carried out by other authors, as shown in Table 7. As can be seen from this table, combination of ICP-OES with DLLME procedures usually leads to detection limits lower than the ones obtained in this work with the same instrumental technique. However, a non-chlorinated extractant solvent was used in the present study, which provides an important advantage over the methodologies proposed [21,44]. On the other hand, the DLLME procedure proposed in this work is simple, avoiding the drying step needed in existing methodologies to evaporate the chlorinated solvent prior to ICP-OES analysis [21,44], or the solidification step to separate the analyte-enriched organic drop from the aqueous solution [45]. Moreover, as an added advantage, the use of a reduced volume of extractant solvent in the proposed method can be also highlighted.

Regarding LIBS, detection of the same target analytes in liquid samples has also been studied by different authors, as shown in Table 8. However, limits of detections

below 1 mg L^{-1} can be hardly achieved without applying some kind of sample treatment or without the use of double pulse LIBS methodology [46]. As can be observed from Table 8, limits of detection slightly below 1 mg L^{-1} can be obtained by sorption of the analytes in ion exchange membranes prior to LIBS analysis [47]. These results can be highly improved if metals in the samples are previously electrodeposited on an aluminum rod [48]. As observed, limits of detection obtained are about 20-30 times lower than the ones achieved in the present work. However, it is worth mentioning that 800 mL aqueous sample was used for electrodeposition of the metals, whereas 9 mL solution was used in this study.

To date, previous studies on the combination of LIBS with liquid-liquid microextraction methodologies for liquid samples analysis have only been carried out by our workgroup. As can be observed from Table 8, the DLLME-LIBS methodology proposed in the present work leads to improved limits of detection compared to our previously proposed methods [49,50]. Moreover, compared to the previously proposed DLLME-LIBS procedure [49], the use of tetrachloromethane as extraction solvent has been avoided.

4. Conclusions

The proposed DLLME procedure, based on the use of a non chlorinated extractant solvent for extraction of Cd, Co, Ni, Pb and Zn as PAN complexes, presented interesting features. This procedure has the advantage of simultaneous preconcentration of all ions with low reagents consumption (65 mg PAN, 70 µL 1-undecanol and 150 µL methanol per sample) and reduced waste disposal. DLLME optimization using a factorial design resulted in a suitable microextraction condition, contributing to the development of simple, rapid and sensitive procedures for Cd, Co, Ni, Pb and Zn determination in different kind of liquid samples.

Association of DLLME with ICP OES (*i.e.*, DLLME-ICP OES methodology) leads to LOQ values at the low µg L^{-1} levels, allowing the analysis of drinking water for quantification of metals at concentration levels allowed by WHO, EPA and EUC (Cd and Zn); regulated by EPA (Pb) or recommended by WHO (Ni).

On the other hand, it has been proved than the sensitive analysis of liquid samples by LIBS, a well known limitation for this technique, could be overcome by its combination with DLLME procedures. According to the results presented in this work, DLLME-LIBS methodology leads to sensitivity improvements that allow the analysis of

small volumes of different liquid samples with low concentration of Ni and Zn, which is not easily affordable by direct LIBS analysis of the samples.

Additionally, by succeeding in the development of analytical methodologies useful for trace analysis of liquid samples with LIBS in the way here proposed (*i.e.*, by combining with microextraction methodologies), it would be possible to profit from the advantages offered by this technique in terms of in-situ and on-line capabilities to develop, in the near future, fast analytical systems based on LIBS to be used, for instance, as early-warning systems for environmental pollution monitoring, which cannot be carried out with conventional spectrochemical techniques such as ICP-OES, ETAAS or ICP-MS.

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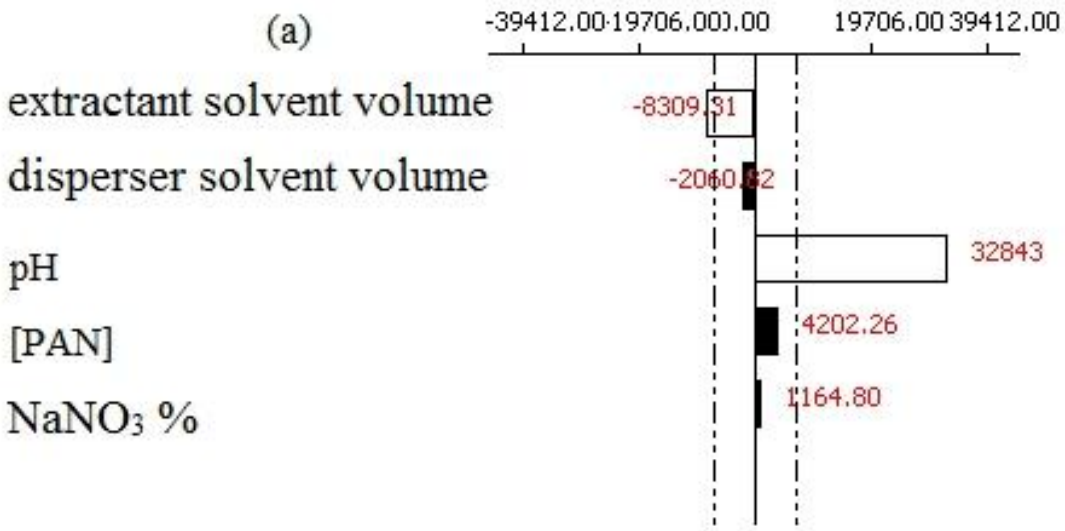
Figure Captions

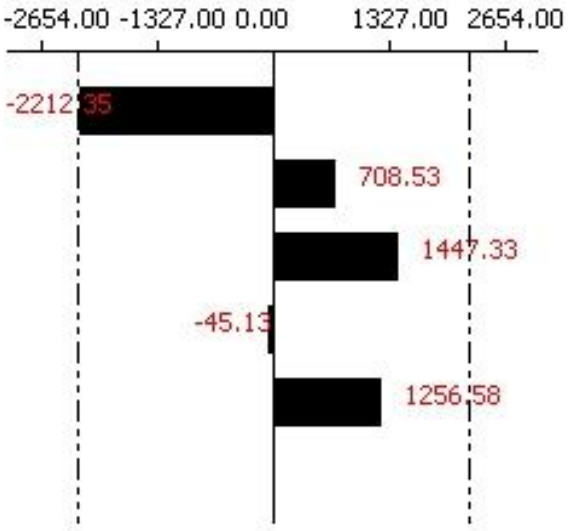
Fig. 1. Pareto charts obtained in the screening study of the experimental factors affecting the DLLME of (a) Cd, (b) Co, (c) Ni, (d) Pb and (e) Zn.

Fig. 2. Signal improvement versus disperser solvent type. Metal concentration in the sample 50 μg L^{-1}; PAN concentration 260 μmol L^{-1}; pH 9.0 (NH_4Cl/NH_4OH), 1-undecanol and disperser solvents volume 70 and 150 μL, respectively. Organic phase was diluted to 100 μL with propanol.

(a)



(b)



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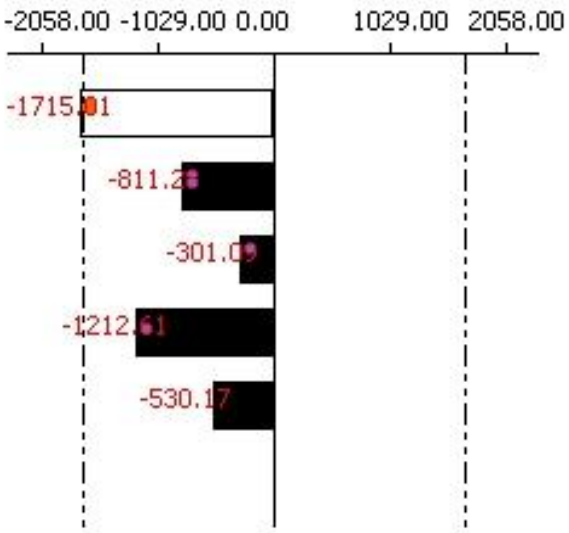
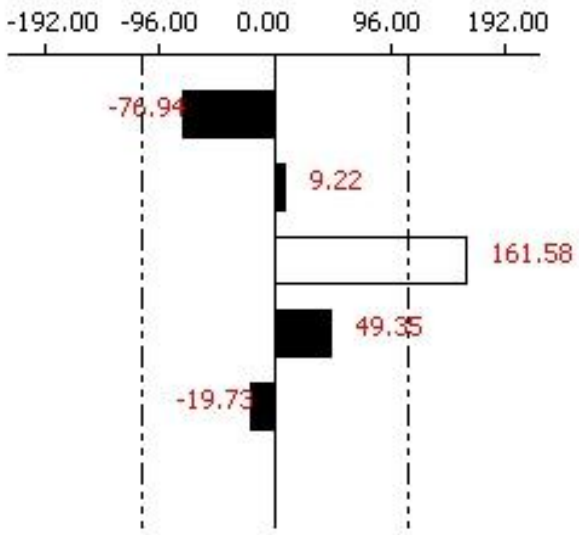


(d)



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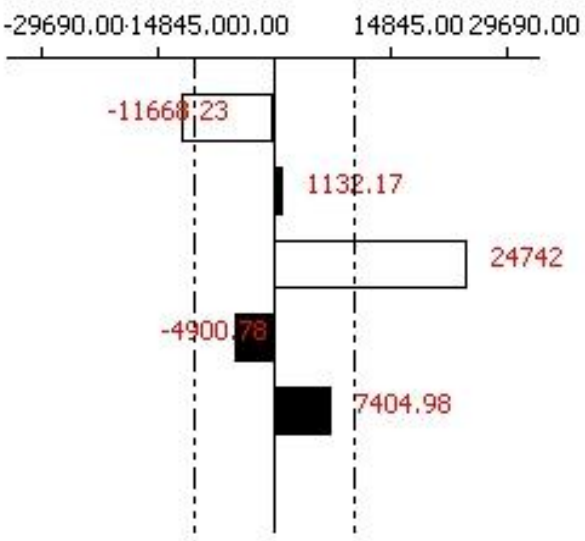

Figure 1a-e

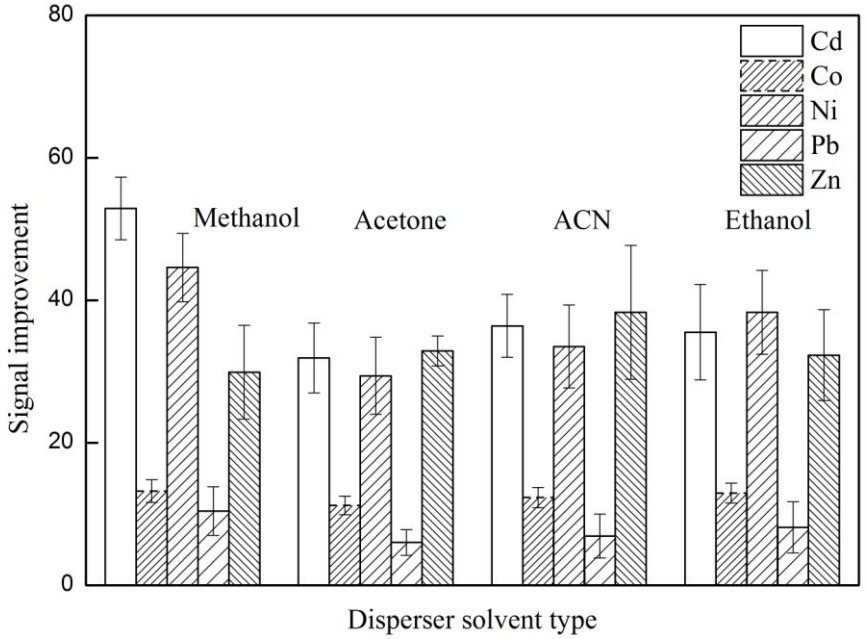

Figure 2

Table1.

Instrumental parameters for ICP OES measurements.

Parameter	Value
RF generator power (kW)	1.2
Plasma gas flow rate (L min^{-1})	15
Auxiliary gas flow rate (L min^{-1})	1.5
Nebulizer type	OneNeb®
Spray chamber type	Cyclonic
Nebulizer gas flow rate (L min^{-1})	0.75
Sample flow rate (mL min^{-1})	0.1
View mode	Axial
Read time (s)	3
Replicates	3
Analytical lines (nm)	Cd II (226.502) Co II (228.616) Ni II (230.299) Pb II (220.353) Zn I (213.857)

Table 2.

Analytical features of DLLME-ICP-OES method for Cd, Co, Ni, Pb and Zn determination.

Parameters	Cd	Co	Ni	Pb	Zn
Linear range (µg L^{-1})	0.0 – 100	0.0 – 100	0.0 – 100	0.0 - 300	0.0 – 200
R^{2a}	0.9965	0.9974	0.9954	0.9934	0.9924
Sensitivity (cts L μg^{-1})[a,b]	2347±398	88±14	355±65	19±7	1014±244
LOD (µg L^{-1})	0.80	3.3	1.1	2.1	1.7
LOQ (µg L^{-1})	2.7	11	3.6	7.0	5.7
Repeatability (RSD %)[c]	5.7	5.0	5.0	8.2	6.5
Relative sensitivity[d]	56	9.5	51	14	51

[a]number of calibration points, n = 6, [b]value ± standard deviation, [c]relative standard deviation, n = 10, Cd, Co and Ni 50 µg L^{-1}, Pb 100 µg L^{-1} and Zn 80 µg L^{-1} ; [d]Sensitivity DLLME-ICP-OES / Sensitivity ICP-OES

Table 3.

Analytical features of LIBS and DLLME-LIBS methods for Cd, Ni and Zn determination.

Parameters	Cd		Ni		Zn	
	LIBS	DLLME-LIBS	LIBS	DLLME-LIBS	LIBS	DLLME-LIBS
Linear range (μg L^{-1})	0.0-1,000	0.0-300	0.0-1,000	0.0-300	0.0-1,000	0.0-500
R^{2a}	0.9711	0.9787	0.9757	0.9824	0.9889	0.9956
Sensitivity (cts L μg^{-1})[a,b]	17 ± 1	164 ± 2	6.7±0.5	45 ± 7	7.8 ± 0.4	51 ± 5
LOD (μg L^{-1})	55	5.2	51	23	35	11
LOQ (μg L^{-1})	183	18	170	78	117	38
Repeatability (RSD %)[c]	-	4.7	-	10	-	6.2
Relative sensitivity[d]	9.6		6.7		6.5	

[a]number of calibration points, n = 5; [b]value ± standard deviation; [c]relative standard deviation, n = 10, Cd, Ni and Zn 0.20 mg L^{-1}**;** [d]Sensitivity DLLME-LIBS / Sensitivity LIBS

Table 4.

Determination of metals in certified reference materials using the proposed DLLME-ICP OES and DLLME-LIBS methods.

Analyte		Found concentration (µg kg^{-1})[a]		Recovery (%)	
Estuarine water (LGC6016)	Certified (µg kg^{-1})	DLLME ICP OES	DLLME LIBS	DLLME ICP OES	DLLME LIBS
Cd	101±2	105±4	105±12	104	104
Ni	186±4	191±7	204±8	103	109
Pb	196±3	199±26	-	102	-
Hard drinking water (ERM® CA011a)	Certified (µg L^{-1})	Found concentration (µg L^{-1})[a]		Recovery (%)	
Cd	4.94±0.23	4.64±0.83	-[b]	94	-
Ni	19.4±1	19.5±1	-[b]	101	-
Pb	24.7±0.5	21.7±1.5	-	88	-
Zn	586±20	599±10	597±35	102	102

[a]value ± standard deviation, n = 3; [b]not detected

Table 5.

Determination of metals in beverage samples by DLLME-ICP OES method.

Samples	Added ($\mu g\ L^{-1}$)	Cd	Co	Ni	Pb	Zn	Cd	Co	Ni	Pb	Zn
		Found concentration ($\mu g\ L^{-1}$)[a]					Recovery (%)				
Drinking water	0.0	-[b]	-[b]	66.7±9.7	-[b]	69.9±6.8	-	-	-	-	-
	25.0	25.6±1.8	27.4±1.0	25.3±0.4	27.4±6.9	23.5±0.6	106	109	101	109	94
	50.0	52.4±2.3	55.7±3.3	48.5±1.0	47.0±4.6	47.5±2.8	107	111	97	94	95
Alcoholic beverage[c]	0.0	-[b]	-[b]	76.3±4.1	-[b]	163±3	-	-	-	-	-
	25.0	23.4±1.3	26.8±3.7	23.8±0.2	4.2±1.2	25.0±0.6	93	107	95	17	100
	50.0	42.7±4.3	54.9±2.0	51.1±2.0	8.5±2.2	53.0±2.3	92	109	102	17	106
Alcoholic beverage[d]	0.0	-[b]	-[b]	698±8.5	-[b]	1290±110	-	-	-	-	-
	25.0	22.7±0.4	24.5±1.8	22.9±0.3	23.2±0.8	26.6±0.4	94	98	92	93	106
	50.0	42.5±3.1	49.4±3.0	48.9±2.4	55.7±2.6	47.3±1.5	93	99	98	111	95
Soft drink	0.0	-[b]	-[b]	49.9±1.7	-[b]	441±13	-	-	-	-	-
	25.0	23.7±1.5	23.4±0.8	24.5±0.9	11.8±0.1	23.4±0.6	95	93	98	47	94
	50.0	45.5±3.7	49.4±1.6	48.3±6.9	25.3±0.8	51.4±5.2	91	98	97	51	110

[a]value ± standard deviation, n = 3; [b]not detected; [c]brand whisky; [d]fruit distillation

Table 6.

Determination of metals in beverage samples by DLLME-LIBS method.

Drinking water	Found concentration (μg L^{-1})[a]	Recovery (%)[b]
Cd	-[c]	-
Ni	73.1±11	109
Zn	60.9±10	87
Alcoholic beverage[d]		
Cd	-[c]	-
Ni	76.5±15	100
Zn	166±11	102
Alcoholic beverage[e]		
Cd	-[c]	-
Ni	713±70	102
Zn	1460±640	113
Soft drink		
Cd	-[c]	-
Ni	49.1±7.1	98
Zn	436±65	99

[a]value ± standard deviation, n = 3; [b]in relation to DLLME-ICP OES results (Table 5); [c] not detected; [d] brand whisky; [e] fruit distillation

Table 7.
Comparison of the proposed methods with other ICP-OES based methodologies for metals determination in water samples

Analytes	Sample Treatment	Sample Treatment Experimental Conditions	LOD ($\mu g\ L^{-1}$)	Ref.
Co, Ni, Cd, Pb	Liquid-liquid microextraction (DLLME) - drying and dissolving	Chelating reagent: BTAC Extractant solvent: Trichloroethylene, 300 µL Disperser solvent: Ethanol, 8.0 mL Sample volume: 40 mL	(0.2-0.6) 0.3 (Cd), 0.2 (Co), 0.2 (Ni), 0.6 (Pb)	[21]
Cu, Cr, Ni, Zn	Liquid-liquid microextraction (DLLME) – drying and dissolving	Chelating reagent: Na-DDTC Extractant solvent: Carbon tetrachloride, 113 µL Disperser solvent: Methanol, 1.00 mL Sample Volume: 10 mL	(0.27-0.55) 0.55 (Zn), 0.4 (Ni)	[44]
Cr, Co, Cu, Mn	Liquid-liquid microextraction (DLLME)- solidification of organic drop - dilution	Chelating reagent: TTA Extractant solvent: 1-undecanol, 140 µL Disperser solvent: Acetone, 2.0 mL Sample volume: 20 mL	(0.1-0.3) 0.2 (Co)	[45]
Cd, Ni, Zn, Pb, Co	Liquid-liquid microextraction (DLLME) - dilution	Chelating reagent: PAN Extractant solvent: 1-undecanol, 70 µL Disperser solvent: Methanol, 150 µL Sample volume: 9 mL	(0.8-3.3) 0.8 (Cd), 3.3 (Co), 1.1 (Ni), 2.1 (Pb), 1.7 (Zn)	This work

BTAC, 2-(2'-benzothiazolylazo)-p-cresol; Na-DDTC, sodium diethyldithiocarbamate; TTA, 1-(2-thenoyl)-3,3,3-trifluoraceton

Table 8.
Comparison of the proposed methods with other LIBS based methodologies for metals determination in water samples

Analytes	Sample Treatment	Sample Treatment Experimental Conditions	LOD ($\mu g\ L^{-1}$)	Ref
Ba, Cd, Cr, Cu, Pb, Hg, Ni, Ag, Zn	Sorption with ion-exchange membranes	Membrane: poly(styrenedivinylbenzene) copolymer support functionalized by iminodiacetic acid groups. Sample volume: 10 mL	(4.2-2000) 850 (Zn), 210 (Cd), 310 (Ni)	[47]
Cr, Mn, Cu, Zn, Cd, Pb	Electrical deposition on aluminum rod	Deposition voltage: 7.5 V Deposition time: 20 min. Deposition surface (cathode): High purity (99.999 %) aluminum Sample volume: 800 mL	(0.16-1.35) 1.35 (Zn), 0.787 (Cd)	[48]
Zn, Cu, Cr, Mn, Ni	Liquid-liquid microextraction (DLLME) - drying on aluminum surface	Chelating reagent: APDC Extractant solvent: Tetrachloromethane, 100 µL Disperser solvent: without disperser solvent [a] Sample quantity: 9 g	(18-107) 18 (Zn), 107 (Ni)	[49]
Zn, Cu, Cr, Mn, Ni	Liquid-liquid microextraction (SDME) - drying on aluminum surface	Chelating reagent: APDC Extractant solvent: Toluene, 7.5 µL Sample quantity: 9 g	(21-301) 21 (Zn), 189 (Ni)	[50]
Cd, Zn, Ni	Liquid-liquid microextraction (DLLME) - drying on aluminum surface	Chelating reagent: PAN Extractant solvent: 1-undecanol, 70 µL Disperser solvent: Methanol, 150 µL Sample volume: 9 mL	(5.2-23) 11 (Zn), 5.2 (Cd), 23 (Ni)	This work

[a]vortex agitation; APDC, pyrrolidinedithiocarbamate

Highlights

- Environmentally friendly spectrometric method for elemental analysis
- Combination of DLLME with ICP OES and LIBS
- Elemental analysis in beverage samples after microextraction procedure
- Sensitive analysis of liquid sample by LIBS combining it's with DLLME